THE REACTION OF METHYL FREE RADICAL WITH 2-METHYL-3-CHLORO-BUTYRONITRILE AND 2-METHYL-3-CHLOROBUTYRIC ACID; AND THE REACTION OF ZINC WITH THE ISOMERIC 2-METHYL-2-CHLORO -BUTYRONITRILE AND 2-METHYL-2-CHLOROBUTYRIC ACID

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PART I

INTRODUCTION

This investigation was undertaken to determine the products formed when diacetyl peroxide is decomposed in 2-methyl-3-chlorobutyronitrile and 2-methyl-3-chloro-butyric acid. The reaction of zinc with the isomeric 2-methyl-2-chloro-butyronitrile and 2-methyl-2-chloro-butyric acid was also studied.

The methyl free radical is highly reactive and attacks most solvents in which it is liberated. Kharasch and Gladstone[1] found that diacetyl peroxide, when decomposed in acetic acid, isobutyric and chloroacetic acids, removes a hydrogen atom from the alpha carbon of the acid in question and thus gives rise to a free radical of the type R_1R_2C-COOH (where R_1 and R_2 may be hydrogen, methyl or chlorine). The free radical thus formed dimerized to give succinic, tetramethylsuccinic and dichloro succinic acids respectively. Smith[2] also decomposed diacetyl peroxide in ethyl and methyl cyanide and was able to obtain a,a' dimethyl succinonitrile and succinonitrile respectively due to the removal of the alpha hydrogen in each case, producing a free radical analogous to the one indicated by Kharasch, which dimerized

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[1] Kharasch and Gladstone, J. Am. Chem. Soc., 65, 15 (1943).

[2] Smith, Masters Thesis, University Chicago (1945).

to give the desired product.

"This unique selectivity of the methyl free radical which was first observed by Kharasch and Gladstone, and by Kharasch, Jensen and Urry[3] has been verified further by McBay.[4] This holds for all cases studied thus far but it is nevertheless to be accepted with some reservation. There may well exist molecules containing both hydrogen and chlorine[5] in which the latter may more easily be selectively removed. The question thus raised deserves further investigation."[2]

The concept of free organic radical was known as early as Gay-Lussac,[6] for he believed that in cyanogen he had isolated the free (CN·) radical of prussic acid. Bunsen[7] reported the isolation of the free cacodyl radical $(CH_3)_2$ As·) in 1841, and Kolbe[8] supposed that he had obtained the free methyl radical ($\cdot CH_3$) by electrolysis of sodium acetate, (1849). However, through Cannizzaro's emphasis upon the distinction between atoms, radicals and molecules (1864), it eventually became evident that in each of the above cases, dimers rather than

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[3]Kharasch, Jensen and Urry, Unpublished Results.

[4]McBay, Ph. D. Dissertation, University Chicago (1945).

[5]Ekaluo, B., Unpublished Thesis, Atlanta University (1949).

[6]Gay-Lussac, Ann. Chim. Phys., 95, 186 (1815).

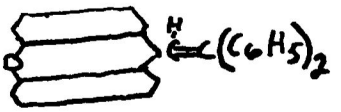
[7]Bunsen, Ann. Chem. Phar., 31, 175 (1839); 371 (1841).

[8]Kolbe, Ann. Chem., 69, 258 (1849).

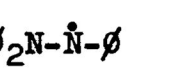
free radicals had been isolated. Frankland[9] utilizing the idea of Bunsen, treated alkyl halides with zinc in sealed tubes; but he, like his predecessors, was unable to isolate free radicals from his products.

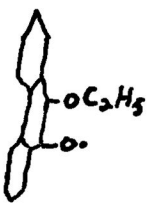
In 1900 Gomberg[10] carried out the first major work on free radicals when he attempted to prepare hexaphenylethane from the reaction of silver and triphenyl methyl chloride. Instead, the triphenylmethane free radical (I) was obtained. Other methods of generating free 9(B,B' diphenylvinyl) xanthyl radical (II) from the corresponding xanthyl perchlorate and phenyl magnesium bromide.

I 

II 

Free radicals involving elements other than carbon are known, such as the triphenyl hydrazyl (III)[12] and 9: ethoxy-10-phenanthroxy radical (IV)[13] which were prepared by Goldschmidt.

III 

IV 

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[9]Frankland, Ann., 71, 171-213 (1849); 74, 63 (1850).

[10]Gomberg, Ber., 33, 3150 (1900).

[11]Ziegler and Cohs, Ber., 55, 2257 (1922).

[12]Goldschmidt, Ber., 44, (1920).

[13]Goldschmidt, Ann., 445, 123 (1925).

"There are several different methods by which organic free radicals can be generated in solution.[14] However, only one of these methods, namely the thermal decomposition of diacetyl peroxide, was used in the work reported here."[4]

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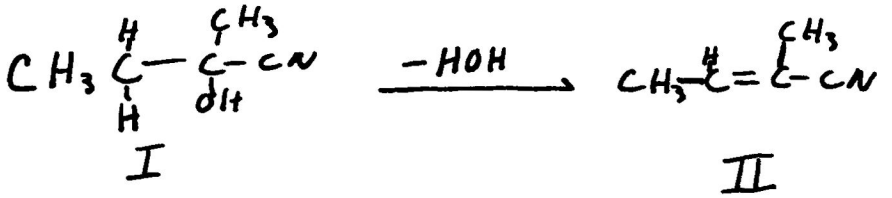
[14] Hey and Waters, Chem. Reviews, 21, 169 (1937).

PART II

THEORETICAL

A great deal of effort was spent in trying to prepare the unsaturated nitrile (II). Although, the hydroxynitrile (I) could be prepared in good yields from ethyl methyl ketone,[15]



I II

it was found that the hydroxynitrile (I) was extremely difficult to dehydrate. As had been reported in the literature, the alpha hydroxynitriles do not undergo dehydration readily to the unsaturated nitrile but instead lose hydrogen cyanide. Also in the case of the alpha hydroxy acids, the ease of dehydration[17] as compared with beta hydroxy acids is much less; this should be expected since carboxyl and nitrile groups maintain the same order of reactivity.

The unsaturated nitrile (IV) was finally prepared by the dehydration of the oxime[18] (III) which could be prepared in

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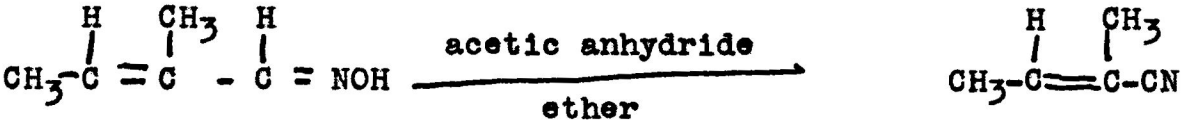
[15]Ultee, Ber., 39 (2) 1857 (1906).

[16]Cook and Limstead, J. Chem. Soc., 956 (1934).

[17]Auwers and Krollpfeifer, Ber., 48, 1394 (1915).

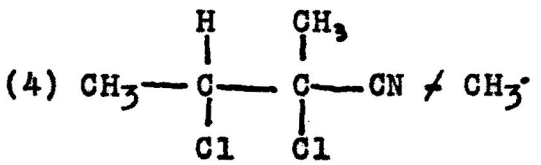
[18]Dollfus, W., Ber., 25, 1920 (1892).

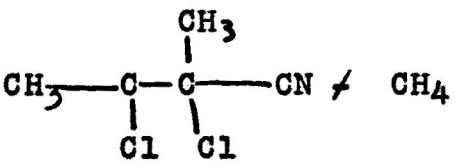
good yields[19] from tiglic aldehyde.

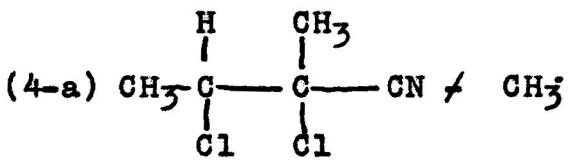


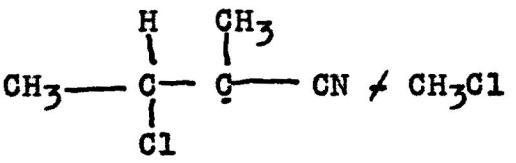
III II

It was found that when dry chlorine was passed into a benzene solution of the olefin (II) 2,3, dichloro-2-cyano-butane was produced in seventy-seven per cent yields. Ekaluo[5] found that when diacetyl peroxide is decomposed in 2-cyano-2,3-dichloro-nitrile, not only did the methyl free radical attack the chlorine in the alpha position (4a) as reported by Kharasch and Gladstone,[1] but the methyl free radical also attacks the hydrogen in the beta position (4). This led to a mixture of hexane derivatives, equations (5), (5-a) and (4-b).









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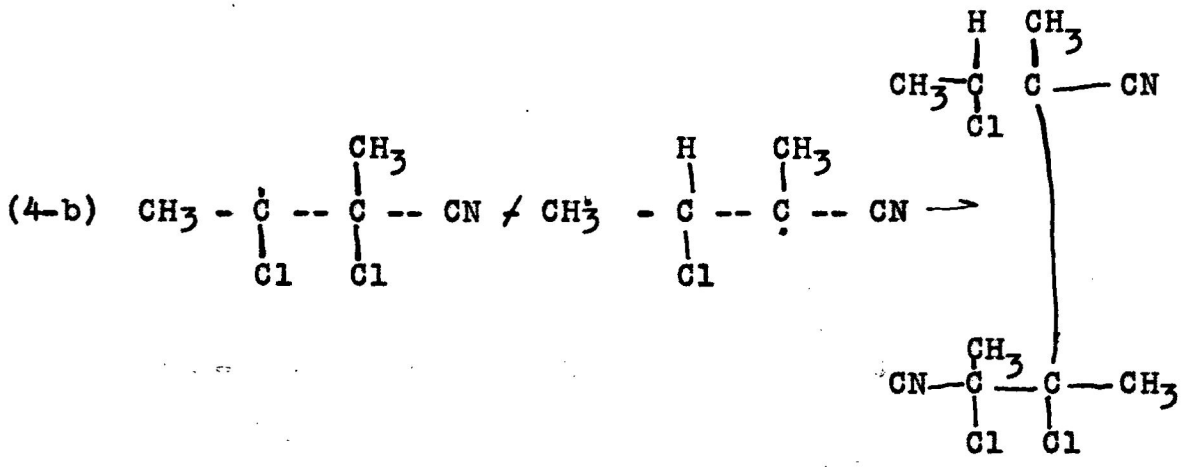
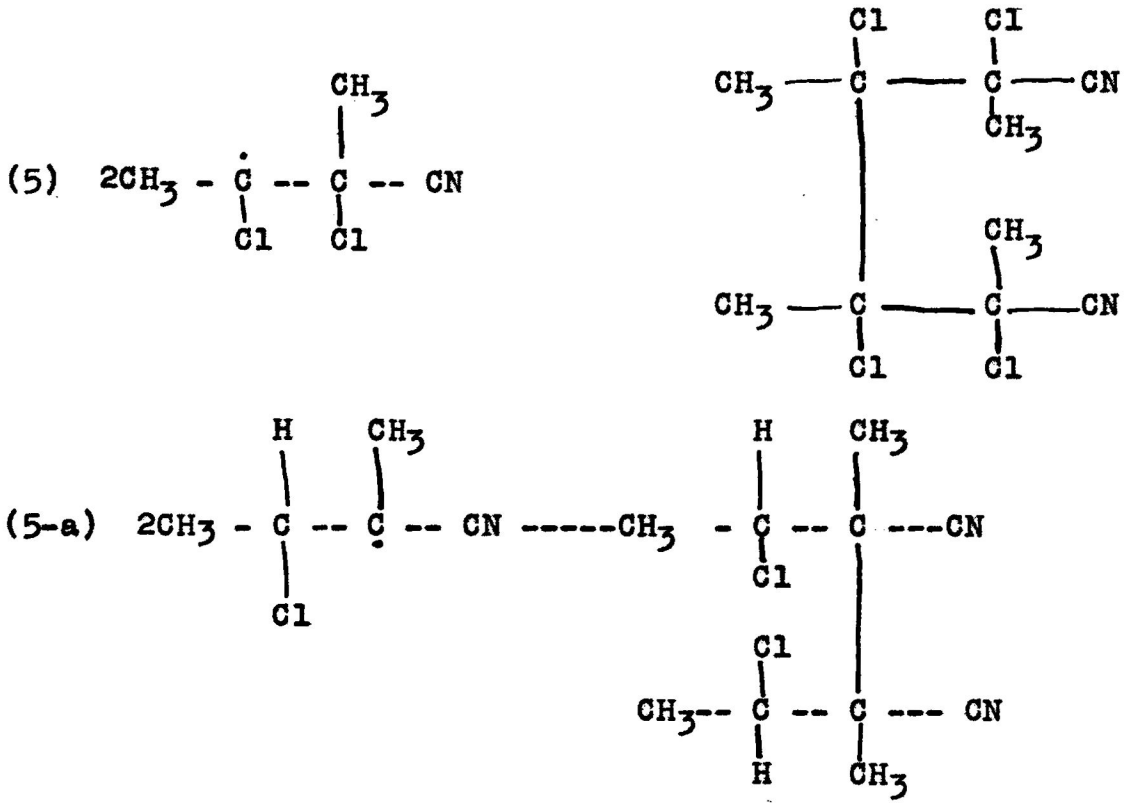
[19] Mowry and Morner, J. Am. Chem. Soc., 69, 1831 (1934).



(4-b)



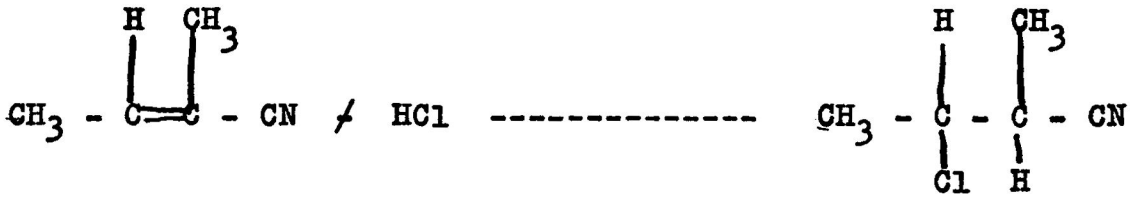
(5)

(5-a)

On the basis of the observation made by Ekaluo, the reactions as indicated above, was not a suitable method for the preparation of the hexane derivative (5-a); since the decomposition of diacetyl peroxide in 2-cyano-2,3,-dichloro-

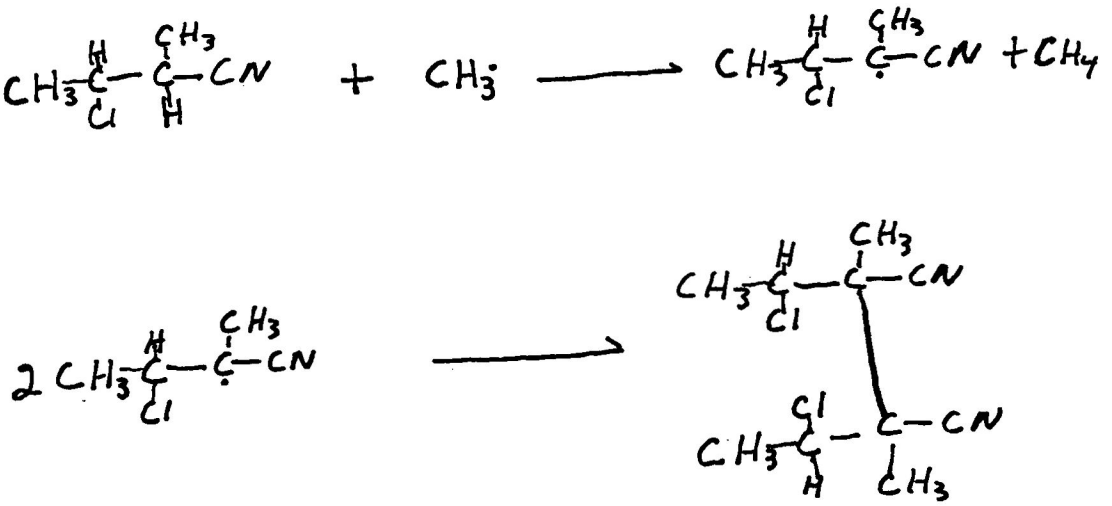
butane produced a mixture of hexane products.

On the addition of hydrogen chloride to 2-cyano-butene-2, the following reaction is expected to take place.



2-Methyl-2-chloro-butyronitrile was prepared in seventy-five per cent yields by saturating a solution of 2-cyano-butene-2, (I), at the temperature of a salt ice bath, with hydrogen chloride. The excess hydrogen chloride was then carefully removed with a cold dilute solution of sodium carbonate. The product was dried over anhydrous sodium sulfate then distilled under diminished pressure.

Diacetyl peroxide (.17 moles) was decomposed at 130°C in 2-methyl-3-chloro-butyronitrile (1.28 moles) as a solvent. The decomposition of diacetyl peroxide proceeded with the formation of very little, if any, methyl chloride or hydrogen chloride, and with the liberation of (.242 moles) of methane, approximately the theoretical amount of methane.



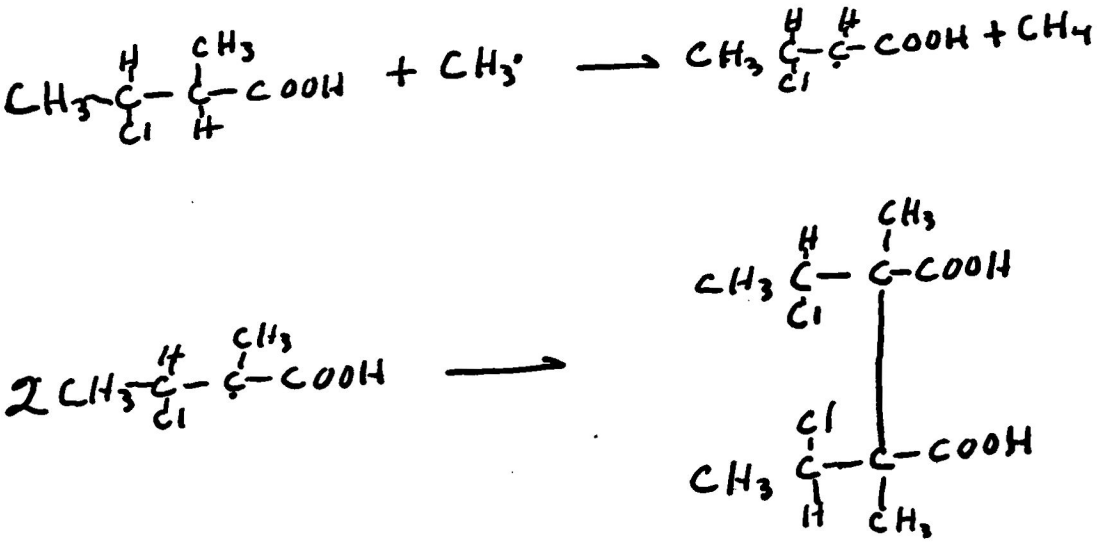
Only ammonium chloride could be obtained from the reaction mixture. Some dimerization is expected on the basis of the theory,[1,2,3,4] although, no dimer was actually isolated. The fact that no methyl chloride or hydrogen chloride was detected during the process of the reaction and approximately the theoretical amount of methane was collected is supporting evidence of the selectivity[1,2,3] of the methyl free radical. If the attack had been in the beta position either methyl chloride, hydrogen chloride or both would have been expected. The removal of the beta hydrogen could have led to the loss of hydrogen chloride and the attack of the methyl free radical on the beta chlorine could have led to the formation of methyl chloride. Thus, it can be concluded with little doubt that the attack was predominantly on the alpha hydrogen.

No explanation is possible at present by which the decomposition of diacetyl peroxide in 2-methyl-3-chloro-

butyronitrile leads to the formation of ammonium chloride.

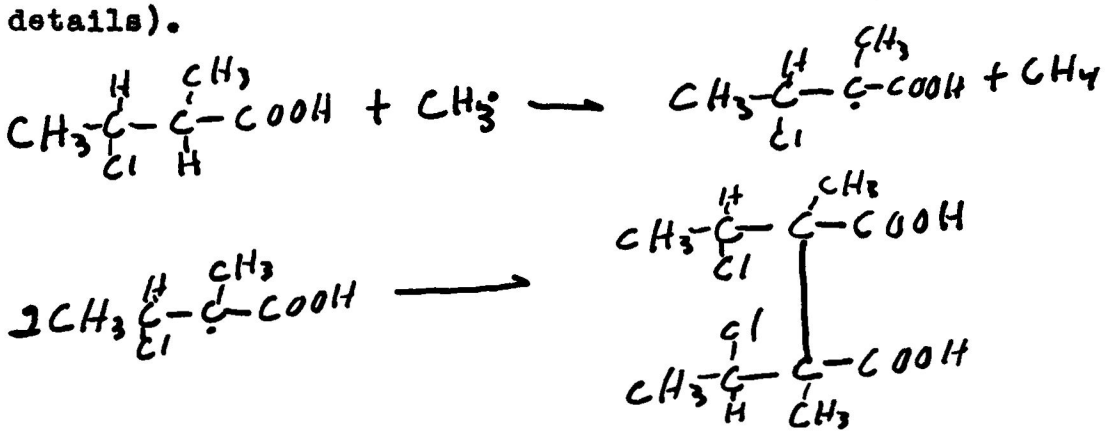
It is understandable that the nitrile group in some way takes part in the reaction when diacetyl peroxide is decomposed in 2-methyl-3-chloro-butyronitrile; since ammonium chloride was isolated from the reaction. However, there is no evidence that the methyl free radical itself attacks the cyanide group; on the other hand Hanby and Waters[20] report that when phenyldiazonium chloride is decomposed in methyl cyanide, a substituted imine, CH_3 CCl NØ, is formed.

If the same order of reactivity is maintained in beta chloro substituted butyric acids as in the acids reported by Kharasch and Gladstone[1] and Kharasch, Jensen and Urry[3] it is expected that the methyl free radical will remove the alpha hydrogen from 2-methyl-3-chlorobutyric acid.



[20]Hanby and Waters, J. Chem. Soc., 131, 1792 (1930).

It was observed in the experiment with diacetyl peroxide and 2-methyl-3-chloro-butyric acid that the methyl free radical attacked the alpha hydrogen according to the theory[1,2,3]. This was concluded on the basis that no methyl chloride or hydrogen chloride was detected and approximately the theoretical amount of methane was collected. However, the expected succinic acid derivative was not isolated from the reaction. Only a syrupy liquid which boils at 110°-125° at .5 to 1 mm. pressure that contained one half the theoretical amount of chlorine was isolated. (See experimental for details).



An effort to determine the exact nature of this product failed. However, on the basis of the analysis this was either a mixture or entirely a new product, possibly a tetramer.

Many attempts have been made wherein metallics such as silver, lead, magnesium, copper and zinc when reacted with halogen containing acids or esters results in coupling. Some of the early reactions with the use of silver were

carried out by Hell[21] who reacted finely divided silver with ethyl bromoisovalerate and ethyl bromopropionate to get the corresponding adipic and succinic derivatives respectively. Ince[22] in 1895 prepared adipic acid by the reaction of gamma iodo propionic acid with copper. The reaction of lead with bromoethyl acetate was carried out by Damler[23] in the preparation of ethyl succinate. It must be noted that the reaction of silver and lead with halogen substituted acids or esters involves a complex type of reaction. Hell found that not only the expected adipic and succinic derivatives were obtained when silver was reacted with ethyl bromoisovalerate and ethyl bromo propionate, but a number of other products. For example, when silver is reacted with ethyl bromopropionate, acrylic acid, pyrocinchonic anhydride are obtained. These results show that the action of silver and lead on halogen containing acids or esters is analogous in mechanism to the action of silver on ethyl bromobutyrate.[24] The reaction with copper seems to be more clear-cut since predominantly a single product is isolated as in the case of the reaction of gamma iodo propionic acid to form adipic

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[21]Hell and Rothberg, Ber., 22, 60 (1889).

[22]Ince, W. H., Soc., 67, 159 (1895).

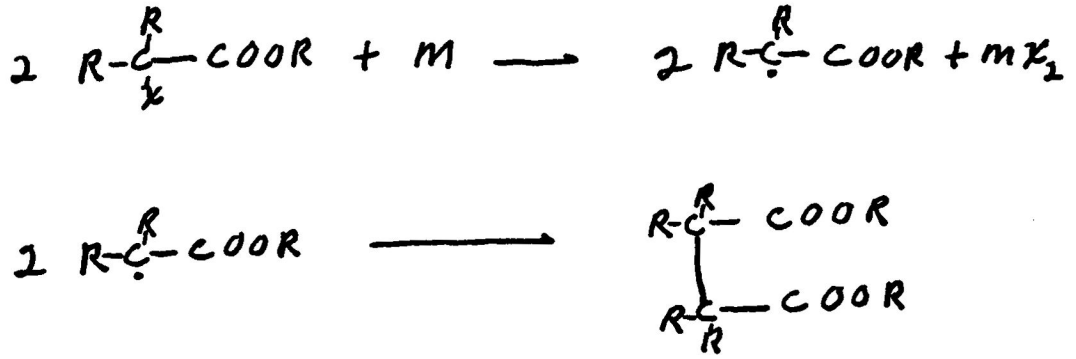
[23]Damler, Ber., 20, 203-204.

[24]Hell and Mulhauser, Chem. Abst., 542 (1880).

acid.

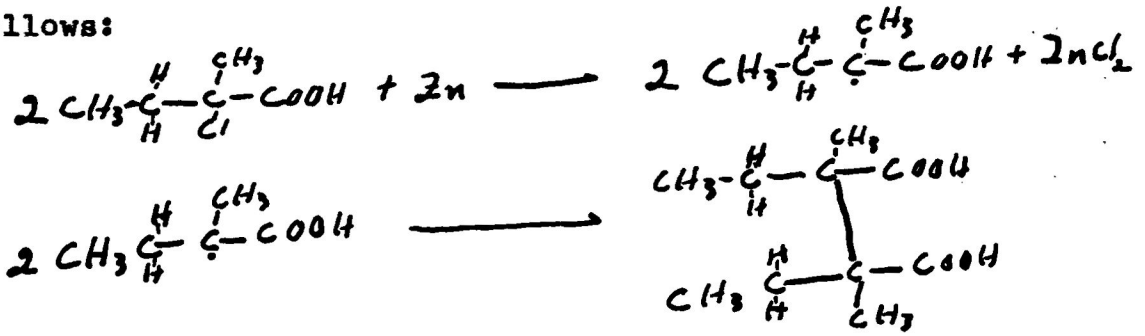
$$2ICH_2CH_2COOH + Cu \text{ ----- } COOH(CH_2)_4COOH + CuI_2$$

A series of coupling reactions using zinc, were performed by Shorige and Co-workers[25] and the reaction of magnesium with halogenated ester was carried out by Barataff[26]. The reaction of halogen containing acids or esters with the metals mentioned previously is of the type as follows:



Where X is a halogen atom and M is the metal.

In the work carried out here 2-methyl-2-chloro-butyric acid and 2-methyl-2-chloro-butyro-nitrile were reacted with zinc. It was expected that the reactions would proceed as follows:



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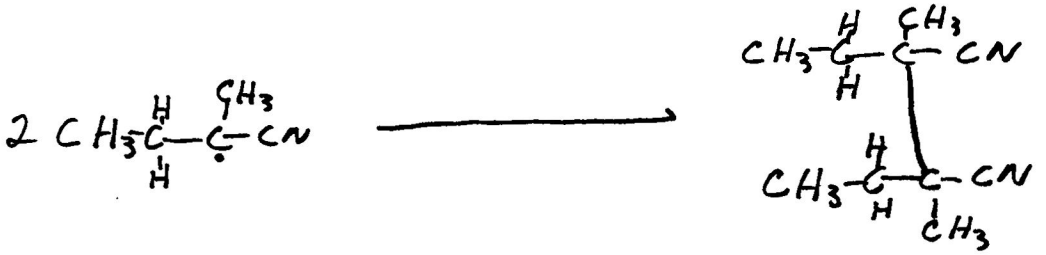
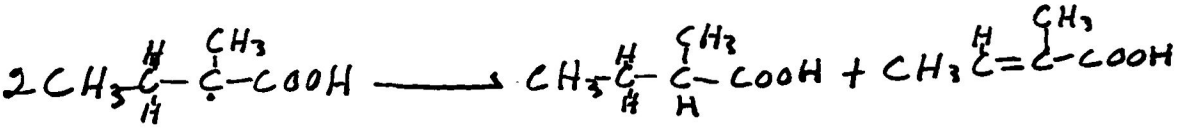
[25]Shorige and Co-workers, J. Am. Chem. Soc., 70, 946 (1948).

[26]Barataff, J. pr. Chem. (2) 357.

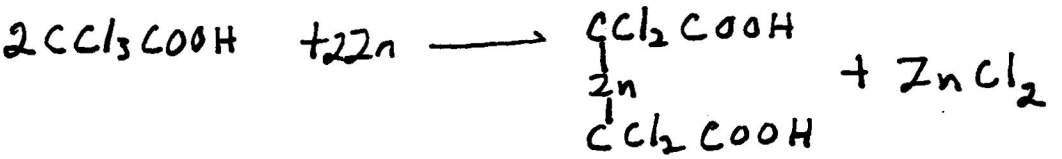


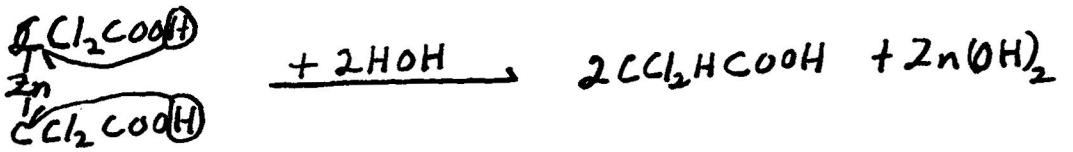
Inasmuch as the nitrile and carboxyl groups maintain the same order of reactivity it was supposed that the same type of reaction would occur in each case. The general procedure was to reflux the halide with zinc while heating for twelve hours in n-propyl alcohol. In each case no succinic acid or succinonitrile derivative was isolated from the reaction mixture. However, the reaction proceded with disproportionation resulting in the formation of tiglic acid and 2-cyano-butene-2 respectively.



In the case of the acid the reaction with zinc provides a method of synthesizing tiglic acid since the yields are as high as forty per cent.

Doughty and Lacoss[27] studied the reaction of trichloroacetic acid with zinc in aqueous solution and found that reduction occurred instead of coupling, as indicated by the following reaction.





There is an organo-metallic compound formed as an intermediate and the two label hydrogens of the carboxyl groups causes a reduction at the positions of the zinc attachment (II). There were no indications of reduction when zinc is reacted with 2-methyl-3-chloro-butyric acid or 2-methyl-2-chloro-butyronitrile.

The reaction of zinc with 2-methyl-3-chloro-butyric acid or 2-cyano-3-chloro butane, may permit a Friedel-Craft type of reaction wherein the zinc chloride can as aluminum chloride react as a Lewis acid. The reaction may proceed as follows:

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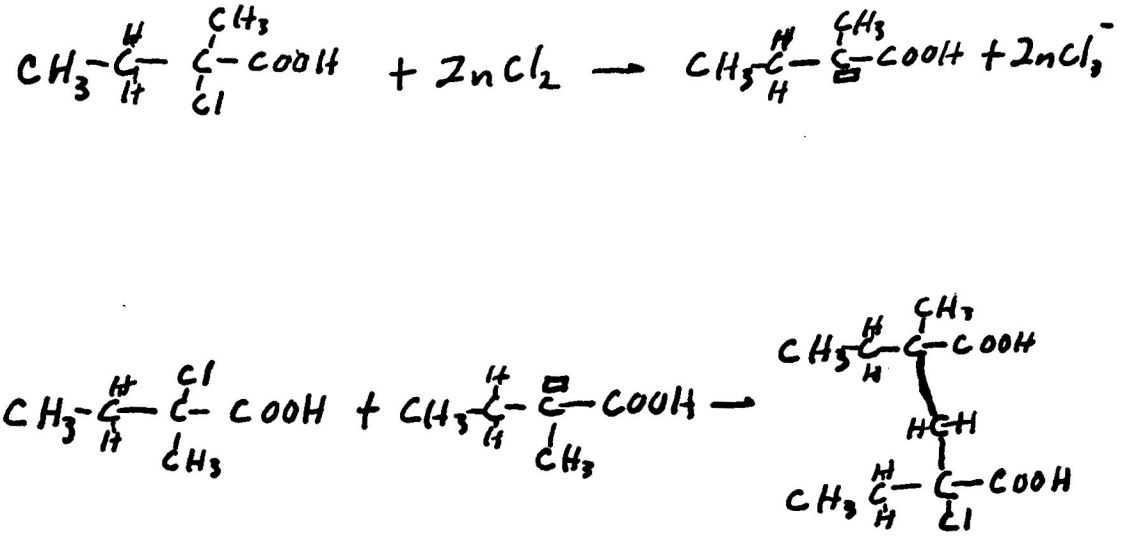
[27] Doughty and Lacoss, J. Am. Chem. Soc., 51, 853 (1929).



However, there was no observed evidence that the above reaction took place.

Hass and McBee,[28] and Whittmore and Popkins[29] have been able to carry out coupling reactions using zinc and aliphatic disubstituted halogen compounds. However, there has been no successful coupling obtained by the reaction of zinc and aliphatic monosubstituted halogen acids or nitriles reported in the literature.

THE REACTION OF METHYL FREE RADICAL WITH 2-METHYL-3-CHLORO-BUTYRONITRILE AND 2-METHYL-3-CHLORO-BUTYRIC ACID

In the work carried out here the reaction of the methyl free radical with 2-methyl-3-chloro-butyronitrile is

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[28]Hass and McBee, Ind. Eng. Chem., 20, 1178 (1936).

[29]Whittmore and Popkin, J. Am. Chem. Soc., 63, 124 (1941).

discussed. The methyl free radical was generated by the thermal decomposition of diacetyl peroxide.

The Decomposition of Diacetyl Peroxide.--The decomposition of diacetyl peroxide in organic solvents is assumed to take place in the following manner. In the first step, the peroxide breaks down into carbon dioxide, a free acetoxy radical and a methyl free radical. In the second step, it is postulated that a methyl free radical reacts with a molecule of solvent to produce a molecule of methane, and a residual free radical of the solvent molecule. In the third step, the two residual radicals dimerize,[1]

I. $2CH_3C\text{-}OO\text{-}C\text{-}CH_3 \quad 2CO_2 \quad 2CH_3C\text{-}O \quad 2CH_3$

II. $2CH_3^{\bullet} + 2UH \quad 2CH_4 + 2U^{\bullet}$

III. $U^{\bullet} + U^{\bullet} \quad U\!:\!U$

where U is an organic residue.

The Decomposition of Diacetyl Peroxide In 2-Methyl-3-Chloro-butyro-nitrile.--In a series of experiments it has been found that a tremendous amount of polymerization occurs when diacetyl peroxide is decomposed, (see Table I and experimental part) below the boiling point of the nitrile, 120°C. In a typical run in which 0.713 moles (84.2 grams) of diacetyl peroxide was decomposed in 365.8 grams of 2-cyano-3-chlorobutane no methyl chloride or hydrogen chloride was detected. A mixture of methyl acetate (1.5 grams), 2-cyano-3-chlorobutane and 2-methyl-3-chloro-

butyronitrile was collected in the cold trap. The only new material that could be isolated from the reaction mixture was ammonium chloride. (See experimental part for identification).

TABLE I

DECOMPOSITION OF DIACETYL PEROXIDE IN 2-CYANO-3-CHLORO-BUTANE 120°

Experiment I.

Reactants	M.W.	Grams	Moles
Diacetyl Peroxide	116	84.2	.713
2-cyano-3-chloro-butane	118	365.8	3.10
Products:			
Methane, S. T. P.	16.1	14.0	.875
Methyl chloride	50.5		
Carbon dioxide	44.0	31.5	.828
Resin		66.0	
Dimer	236		
Methyl acetate	74	2.2	.034

Experiment II.

Reactants	M.W.	Grams	Moles
Diacetyl Peroxide	116	20.2	.17
2-cyano-3-chloro-butane	118	149.0	1.28
Products:			
Methane, S. T. P.	16.1	3.8	.242
Methyl chloride	50.5		
Carbon dioxide	44.0	13	.285
Resin		37.0	
Dimer	236.0		
Methyl acetate	74.0	1.2	.018

Decomposition of Diacetyl Peroxide In 2-Methyl-3-chloro-butyric Acid.--When diacetyl peroxide was decomposed in 2-methyl-3-chloro-butyric acid, (see experimental part also Table II) methane, carbon dioxide and a small amount of methyl acetate were formed. No methyl chloride or hydrogen chloride was detected just as was the case of the nitrile. The reddish, oily residue obtained did not crystallize on standing. It was separated into two fractions by distillation under diminished pressure. Analysis of each fraction indicated that it contained approximately one half the theoretical amount of chlorine expected for the dimeric product.

TABLE II

DECOMPOSITION OF DIACETYL PEROXIDE IN 2-METHYL-3-CHLORO-BUTYRIC ACID 130°

Experiment I.

Reactants	M.W.	Grams	Moles
Diacetyl Peroxide	116	24.9	.211
2-methyl-3-chloro-butyric acid	137	277.5	2.03
Products:			
Methane, S. T. P.	16.1	3.9	0.2437
Methyl chloride	50.5		
Carbon dioxide	44.0	18.2	418
Resin		48.0	
Dimer	272		
Methyl acetate	74	1.1	.017

Experiment II.

Reactants	M.W.	Grams	Moles
Diacetyl Peroxide	116	36.4	.314
2-methyl-3-chloro-butyric acid	137	239.5	1.8
Products:			
Methane, S. T. P.	16.1	3.8	.2436
Methyl chloride	50.5		
Carbon dioxide	44.0	20.6	.465
Resin		30.5	
Dimer	272		
Methyl acetate	74	1.0	.013

THE REACTION OF ZINC WITH 2-METHYL-2-CHLORO-BUTYRONITRILE AND 2-METHYL-2-CHLOROBUTYRIC ACID

The Reaction of Zinc with 2-Methyl-2-chloro-butyronitrile.--When 2-methyl-2-chloro-butyronitrile is reacted with zinc (12 mesh) under the conditions indicated in the experimental part, disproportionation occurs resulting in the formation of 2-cyano-butene-2. No dimeric product was isolated from the reaction mixture. Due to the rapidity with which the unsaturated nitrile polymerized the percentage yield of unsaturated nitrile was not obtainable.

The Reaction of Zinc with 2-Methyl-2-chloro-butyric Acid.--It was observed (see experimental part) when zinc (12 mesh) was reacted with 2-methyl-2-chloro-butyric acid disproportionation occurs, as in the case of the corresponding nitrile, resulting in the formation of tiglic acid in forty per cent yields. The tiglic acid which was

isolated was identified on the basis of mixed melting point and molecular weight determinations.

PART III

EXPERIMENTAL

PREPARATION OF ALPHA METHYL ALPHA HYDROXY BUTYRONITRILE[16]

Sodium bisulfite (475 gms. or 2.5 moles) dissolved in 200 cc. of water was added dropwise to 390 grams of ethyl methyl ketone contained in a three-neck 3 liter round bottom flask equipped with a stirrer, dropping funnel and a reflux condenser. The flask was packed in an ice-salt bath and a temperature of 10° - 20°C was maintained throughout the entire reaction period. The reaction mixture was vigorously stirred with a mechanical stirrer. The mixture was stirred for an additional half-hour after the addition of all of the sodium bisulfite solution. A saturated solution of 294 grams (5.8 moles) of sodium cyanide was added very slowly to the bisulfite addition compound and stirring continued for another hour. The mixture was allowed to stand for thirty minutes and the oily layer (top) separated. The oily layer was neutralized with a few drops of conc. H_2SO_4, dried over anhydrous sodium sulfate, and distilled at reduced pressure.

B.P. - 80° C/5 mm $\qquad$ $N_D^{22^{\circ}}$ - 1.4135

Wgt. - 274.8 grams

Yield - 52.3%

Theoretical - based on ethyl methyl ketone - 524 grams.

PREPARATION OF ALPHA METHYL ALPHA CHLOROBUTYRONITRILE

Three hundred grams of alpha methyl alpha hydroxybutyronitrile dissolved in 300 ml of dry benzene was added dropwise, with vigorous stirring to 453 grams of phosphorus pentachloride contained in a three-liter three-neck flask. The mixture was heated to 50°C until the evolution of HCl ceased (6 hours). The reaction mixture was poured slowly into twice its volume of ice water and stirred. The benzene and aqueous layers were separated. The benzene layer was dried over anhydrous sodium sulfate, after which the benzene was removed, and the residue fractionally distilled at reduced pressure.

B. P. - 55° - 65° C/32 mm - Wgt. 81.9 grams

Yield - 81.9 grams N_D^{20} - 1.41551

PREPARATION OF ALPHA METHYL ALPHA CHLORO BUTYRIC ACID[30]

Alpha chloro alpha methyl butyronitrile (157 grams) was refluxed with 300 cc of concentrated 37% HCl for six hours. Upon cooling, white crystals of ammonium chloride settled out and the oily acid separated out as a separate layer. The acid layer was separated and dried over anhydrous sodium sulfate, and distilled at reduced pressure.

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[30]Servais, Rec. Trav. Chem., 20, 58-59 (1901).

I. B. P. - 120° - 125° C/36 mm - Wgt. 151.3 grams

151.3 g Wgt. of methyl alpha chloro butyric acid

Yield theoretical - 182 grams, based on nitrile

Yield 83.1%

N_D^{21} - 1.45670

PREPARATION OF 2-CYANO-2-BUTENE FROM TIGLIC ALDEHYDE[18]

Tiglic aldoxime[19] (200 gm) freshly distilled was dissolved in three times its weight of a solution of acetic anhydride in ether. The mixture was allowed to stand at room temperature over night, and was carefully neutralized with a saturated solution of sodium carbonate and extracted with ether. The ether extracts were combined and dried over sodium sulfate. The nitrile distilled at 30°C under 42 mm. The yield was seventy-six per cent of the theoretical.

PREPARATION OF 2-CYANO-3-CHLORO-BUTANE

Without distillation the ether solution of the crude 2-cyano-2-butene, after the ether solution had been dried, was saturated with dry hydrogen chloride until hydrogen chloride ceased to be absorbed. The reaction was carried out in an ice salt bath while stirring mechanically. After which the product was washed free of excess hydrogen chloride with a five per cent solution of sodium carbonate, then washed with water and dried over anhydrous sodium sulfate. The product distilled at 62-63°C 10/mm. The light yellow

oil gave the following constants:

$N_D^{21^\circ}$ - 1.4357 literature, $N_D^{20^\circ}$ - 1.4359

Anal. Calcd. for $C_5 H_7 N Cl$: Cl, 30.20.

Found: Cl, 30.00; 29.64%.

PREPARATION OF 2-METHYL-3-CHLORO BUTYRIC ACID

2-Cyano-3-chloro-butane was refluxed with three times the theoretical amount of commercial hydrogen chloride (thirty-five per cent) using a mechanical stirrer while heating in an oil bath at 95°C for 12 hours B. P. 95-97°C at 9 mm.

$N_D^{21^\circ}$ - 1.4480

Anal. Calcd. for $C_5H_7ClO_2$: Cl, 26.00.

Found: 25.88; 25.95%.

DECOMPOSITION OF DIACETYL PEROXIDE IN 2-CYANO-3-CHLORO-BUTANE

The diacetyl peroxide was made, weighed and decomposed according to the method by Kharasch and his Co-workers[4] which is a modification of the method used by Gambarjan.[31]

A solution of 20.2 gms. (0.17 mole) of diacetyl peroxide dissolved in 105 gms. of 2-cyano-3-chloro-butane, was slowly dropped into 49.0 gms. of the nitrile heated to 120°C in a one liter reaction flask. The addition which lasted for an

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[31]Gambarjan, Ber., 42, 4010 (1909).

hour was so regulated as to secure a fairly steady stream of bubbles. Carbon dioxide (13.00 gms.) was absorbed in soda lime tubes and 5.6 liters of gas identified as methane by a mol. wt. determination (mol. wt. 16.1) was collected over water at 17°C. The system was swept with dry air. A small amount of low-boiling liquid (3.2 gms.) identified as a mixture of methyl acetate, 2-cyano-butene-2 and 2-methyl-3-chloro butyronitrile was collected in the cold trap. The mixture was identified by fractional distillation and refractive index.

Distillation of the residue in the reaction chamber yielded 97.0 gms. of solvent, at 62°C 10/mm from the reaction chamber, and 37.0 gms. of resinous dark residue was left. If the residue is allowed to stand for 12 hours, and in some instances without standing, a white crystalline substance precipetates out. On analysis this substance was found to be ammonium chloride. The residue was allowed to stand after the solvent had been removed. After standing for several days in the dark a crystalline white precipitate collected at the bottom and along the sides of the flask. The crystals were removed and analyzed. The analytical results were the same given by the crystals removed from the cold trap, which was ammonium chloride. Extraction of the residue with water followed by evaporation of the extract and cooling results in the precipitation of ammonium chloride. Attempts were made to distill the residue but only

polymerization resulted.

DECOMPOSITION OF DIACETYL PEROXIDE IN 2-CYANO-3-CHLORO-BUTYRIC ACID

A solution of twenty-four and nine-tenth grams (0.211 moles) of diacetyl peroxide dissolved in 277.5 gms. of 2-methyl-3-chloro-butyric acid, was slowly dropped into 77.5 gms. of the acid heated to 130°C in a one liter reaction flask. The addition which lasted for an hour was so regulated as to secure a fairly steady stream of bubbles. Carbon dioxide (18 gms.) was absorbed in soda lime tubes and 5.6 liters of gas identified, as methane by molecular weight determination, (mol. wgt. 16.1) was collected over water at 23°C. The system was swept out with dry nitrogen. A small amount of low-boiling liquid (1.1 gms.) identified as methyl acetate was collected in the cold trap.

Distillation of the residue in the reaction chamber yielded 231.0 gms. of solvent, boiling at 95°C under 9/mm, and 40 gms. of reddish residue was left. After the removal of the solvent the residue in the flask was dissolved in diethyl ether and filtered. Then the ether was removed by use of a pump and vacuum dessicator. The residue was placed in a salt ice bath but no crystals formed. A portion of the residue a red sirupy oil was extracted with ligroin also with acetone and cooled in a salt ice bath but no crystals formed.

The red sirupy oil was then distilled at reduced pressure.

A very light red distillate was collected between 110°-125°C at .5 to 1 mm pressure and 125-135°C at .5-1 mm. both distillates were accompanied by a fine white solid material which was suspended through the distillates. At the side arm of the distilling flask was a small amount of solid material which was not very soluble in ether, ligroin, or acetone even when heated. The material had an amorphous appearance which gave a positive chlorine test and began to sublime around 118°C. The distillate had the appearance of a racemic mixture of the dimer since theoretically there are sixteen isomeric forms. On the basis of the analysis the distillates were either mixtures or entirely new products. The solid material was not sufficient in quantity to permit analysis.

First distillate 110°-125°C

Anal. Calcd. $CH_{12}O_4Cl_2$: Cl, 26.10.

Found: 15.89; 16.80%

Second distillate 125°-135°C

Anal. Calcd. $C_{10}H_{12}O_4Cl_2$: Cl, 26.10.

Found: 12.98; 12.14.

PREPARATION OF 2-CYANO-BUTENE-2

Zinc (16 gms. or .25 moles) was placed in a one liter flask, equipped with a mechanical stirrer, condenser and dropping funnel, containing 100 cc of n-propyl alcohol (five per cent water by volume). Fifty-nine gms. (.5 mole)

2-chloro-2-cyano-butane was placed in the dropping funnel and added slowly to the zinc mixture while stirring. After all the nitrile had been added stirring was continued for 12 hours at 95-100°C, after which the reaction was acidified with five per cent hydrogen chloride. An oil separated out which polymerized in the acid medium. The addition of the acid was to put the gelatinous zinc chloride in solution. On distillation of the oil it was found to boil at 30° under 42 mm. N_D^{28} 1.3980

PREPARATION OF TIGLIC ACID

Zinc (16 gms. or .25 mole) was placed in a one liter flask equipped with a mechanical stirrer, condenser and dropping funnel containing 100 cc of n-propyl alcohol (5% water by volume). 2-Methyl-3-chloro-butyric acid (68 gms. or .25 mole) was slowly added to the zinc mixture while stirring. After all the acid had been added stirring was continued for 12 hours at 95°-100°C after which the reaction was acidified with concentrated HCl. Upon cooling white crystals of tiglic acid precipitated oyt. The crystals were filtered away, washed with cold water and air dried. M.P. 60-61°C. Molecular wgt. determination (Rast method):

Theoretical ---101.

Found ----------101 - 105.

PART IV

SUMMARY AND CONCLUSION

Previous results have shown when diacetyl peroxide was decomposed in 2-methyl-3-chlorobutyric acid and 2-cyano-3-chlorobutane, approximately the theoretical amount of methane was collected; no methyl chloride or hydrogen chloride was detected. In the case of the 2-cyano-3-chlorobutane only ammonium chloride was isolated from the reaction mixture, while in the case of the 2-methyl-3-chlorobutyric acid, a high boiling substance, containing one half the theoretical amount of chlorine for the cleavage of the methyl free radical and the dimerization of the residual radical was obtained. It has been shown also that the reaction of zinc with 2-cyano-2-chlorobutane, and 2-chloro-2-methyl butyric acid results in disproportionation with the formation of 2-cyonobutene-2 and tiglic acid respectively. The latter proved to be a satisfactory method for synthesizing tiglic acid since the yields are as high as forty per cent.

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